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Shear Surface Rheology of Poly(*N*-isopropylacrylamide) Adsorbed Layers at the Air−Water Interface

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ABSTRACT: We investigate the shear surface rheology of a thermosensitive polymer, PNIPAM (poly(*N*-isopropylacrylamide)), adsorbed at the air−water interface using an interfacial stress rheometer. This polymer is characterized by a lower critical solution temperature, LCST, of 32 °C; i.e., PNIPAM chains undergo a coil to globule transition as the temperature is increased above the LCST. We measure a spectacular increase in the surface shear elasticity and viscosity of PNIPAM layers as a function of the temperature around the LCST due to an increase in the amount of adsorbed species as the solvent quality decreases for PNIPAM chains. Moreover, the layers undergo a transition from a Newtonian liquidlike state to an elastic state due to an increase in intermolecular entanglements. We also show that the heating protocols have a strong influence on the rheological properties of the layers. In particular, we show that when the solutions are continuously heated from ambient temperature to well above the LCST, PNIPAM chains can be trapped in a nonequilibrium state at the air−water interface above the LCST. Last, we report on the influence that the PNIPAM bulk concentration and molecular mass have on the surface rheological properties at the air−water interface.

1. Introduction

PNIPAM (poly(*N*-isopropylacrylamide)) is a nonionic thermosensitive polymer characterized by a lower critical solution temperature (LCST) of 32 °C. Below 32 °C, water is a good solvent for PNIPAM, which forms coils due to hydrogen bonds between the acrylamide groups of PNIPAM and the water molecules that solubilize the chains. When solutions of PNIPAM are heated above 32 °C, entropic energy from the water molecules begins to overcome the hydrogen bonding responsible for PNIPAM solubilization, which results in progressive precipitation of the polymer with increasing temperature. A LCST of 32 °C is noteworthy as it coincides with the normal body temperature, and PNIPAM can thus be used to formulate controlled drug delivery systems. For these formulations, understanding the interfacial behavior of PNIPAM chains at a hydrophobic surface such as the air−water or oil−water interface is needed to control the processes involved.

Previously, the interfacial behavior of PNIPAM adsorbed layers at the air−water interface has been studied by mean of surface tension,[1−3] ellipsometry,[4,5] surface light scattering,[6] neutron reflectivity measurements,[7−9] and dynamic surface dilatation rheology.[5,10] The PNIPAM chains have been shown to absorb significantly at the air−water interface in both good and bad solvent conditions.[7,9] When the temperature is increased up to the LCST and above, the adsorbed amount as well the thickness of the adsorbed layer has been shown by Jean et al. to increase significantly.[7,9] Above the LCST, the polymer chains have been observed to form highly heterogeneous thin-liquid films due to the formation of hydrophobic interfacial microgels, resulting in very slow drainage times.[7] Recently, Noskov et al. have studied the adsorption kinetics of dilute PNIPAM solutions (10^{-9}−10^{-1} wt %) at ambient temperature by means of ellipsometry and surface dilatational rheology using the capillary-wave and the oscillating-barrier methods.[5] The authors find nonmonotonic increase of the surface dilatational elasticity with time. Their results, combined with ellipsometric measurements, show that the PNIPAM first adsorbs in flat layers at the air−water interface, resulting in an increase in the surface dilatational elasticity. When interfacial PNIPAM concentrations are increased further, the interface is composed of a concentrated "proximal zone", close to the interface, and a "central zone" composed of long polymer loops and tails protruding into the solution. At this stage, a decrease in the surface dilatational elasticity is witnessed because the surface stress can be relaxed easily through exchange of material between the loops of the central region and the proximal region. However, the shear surface rheology of PNIPAM has not been characterized. This rheological property enables one to probe surface entanglements more directly rather than the exchange of material between the interface and the volume.

In the present paper, we investigate the surface shear rheology of dilute PNIPAM solutions at the air−water interface as a function of temperature using an interfacial stress rheometer built in our laboratory.[11] We observe a spectacular increase of the surface shear elasticity and viscosity as a function of the temperature around the LCST whereas the bulk viscosity of PNIPAM solutions remains low. Moreover, the layers undergo a transition from a Newtonian liquidlike state to an elastic state. We attribute this behavior to the increased amount of adsorbed chains and therefore of the density of the layers. We also show that heating protocols have a strong influence on the rheological properties of the layers. Last, we report on the influence that the PNIPAM bulk concentration and molecular mass has on the surface rheological properties at the air−water interface.

2. Experimental Description

2.1. Materials. PNIPAM, poly(*N*-isopropylacrylamide) (monomeric structure shown in Figure 1), with molecular weights of M_w = 10 250, 39 000, 76 700, 186 800, 465 500, 962 500, and 875 400 g/mol, were purchased from Polymer Source, Inc., and used as received (product numbers P3250, P3270, P2985, P2983, P2173, P2181, and P7140). The polydispersity indexes are respectively 1.12, 1.45, 1.93, 2.63, 4.9, 5.16, and 2.6. Solutions of 0.1 and 1 g/L PNIPAM in water were prepared by dissolving the desired

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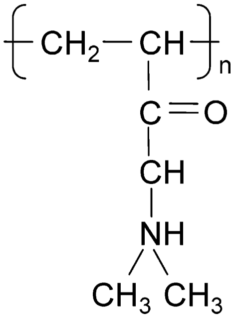

Figure 1. Chemical formula of PNIPAM monomer unit.

amount of PNIPAM in pure water (purified through Milli-Q Academic A10, conductivity 18.2 Mohm) and stirred overnight prior to experimental use.

2.2. Surface Shear Rheological Measurements. The surface shear rheology of the layers formed by PNIPAM chains is studied with an interfacial stress rheometer, which is described in detail in the references from Brooks et al.[11] In this setup, a Teflon-coated magnetic needle is floating at the air−water interface inside a glass channel and is subjected to an oscillatory magnetic force generated by a pair of Helmoltz coils. The resulting motion of the needle was detected using an optical microscope and a photodiode array that detects the shadow of the needle behind a light source. The oscillating magnetic field induces a sinusoidal motion of the rod at the same frequency but different in phase. The rod's displacement divided by the distance between the needle and the glass wall defines the interfacial strain. From the time-dependent surface strain response to the applied surface stress created by the magnetic field, one is able to determine the phase lag, ϕ, between the stress and the strain as well as the ratio of their amplitudes, AR. From AR and ϕ, and after calibration of the setup, one is able to measure the complex shear surface modulus G^*, which is a complex number defined as the sum of two contributions: $G^* = G' + iG''$, where G', the storage modulus, represents the elastic properties and G'', the loss modulus, describes the viscous behavior. For all the solutions investigated, the interfacial shear moduli exhibit no dependency on the strain amplitude over strains ranging from 0.001 to 0.03, indicating that we conducted measurements in the linear viscoelastic regime. In the case of the frequency sweep experiments, the frequency ranges from 0.05 to 1 Hz.

The compression experiments reported in section 3.3.1 were performed by using Teflon barriers attached to the trough. The displacement of the barriers was performed using a motor controlled by a computer (KSV software).

2.3. Temperature Control. The solution was poured into a Langmuir trough, which was equipped with circulation channels integrated into the walls of the trough enabling us to control the temperature of the solution with a thermostat bath. In other cases the solution was kept in a smaller trough with a temperature regulated by maintaining the trough in a water bath at the desired temperature. Results obtained with both temperature control methods were reproducible and consistent with each other. The temperature of the solution was measured using a platinum resistance as well as a thermocouple dipped into the solution. We investigated three types of temperature cycles, which are described in section 3.2 schematically portrayed in Figure 6a.

2.4. Bulk Viscometry. The bulk viscosity of the solutions was measured as a function of temperature using a Bohlin CVOR 150 rheometer. Experiments were performed in a plate−plate configuration using a 30 mm diameter plate. The gap between the two planes was set to 100 μm. This gap was chosen to obtain accurate measurements of our relatively low-viscosity solutions. We imposed the stress, which was increased and decreased, for each temperature between 0.05 and 5 Pa. For each stress value the corresponding viscosity was measured after leaving the sample for 100 s under shear. For all temperatures, within the stress range investigated, the viscosity was found to be independent of the applied stress, indicating a Newtonian behavior. To avoid any disturbances due to evaporation of the sample during our experiments, we replaced the liquid which was squeezed out of the gap by a fresh amount of liquid from the same solution at every three temperature points. This protocol was applied twice upon increasing temperature and once upon decreasing it. For these three experiments we always obtained similar results. Control experiments with pure water in the same temperature range were performed, and the values we found were in accord with those reported in the literature.

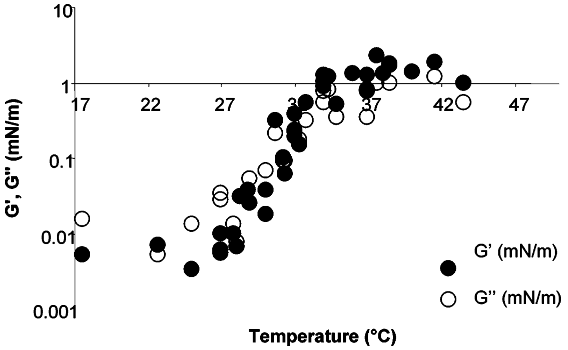

Figure 2. G' (full circles) and G'' (open circles) as a function of temperature for a PNPAM solution of concentration 1 g/L and molecular weight 962 500 g/mol.

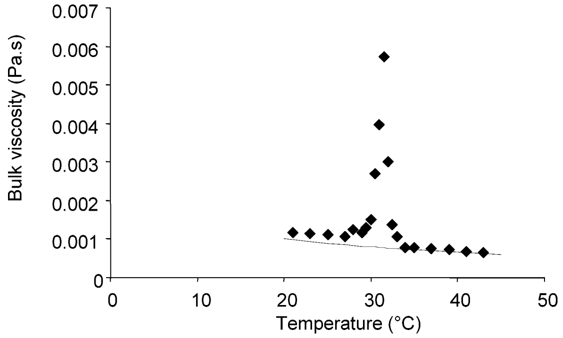

Figure 3. Bulk viscosity of PNIPAM solutions (1 g/L).

3. Results and Discussion

3.1. Influence of the Temperature−Structure of the Layers. The storage and loss shear surface moduli, respectively G' (full circles) and G'' (open circles), of PNIPAM solutions (1 g/L, $M_w = 962K$ g/mol) were measured as a function of temperature from 17 to 45 °C (Figure 2, note the semilogarithmic scale). The protocol used, called process 1 (see section 3.2.1), consists of heating the solution to the desired temperature and performing a measurement after 1 h. The solution is then heated to a higher temperature, typically 1 or 2 °C higher, and the measurement is made 1 h later. This protocol is repeated until the temperature reaches 45 °C. G' and G'' have low values in the range of 5×10^{-3} mN/m from 17 to 27 °C and then increase to 1.5 mN/m (i.e., by nearly 3 orders of magnitude) as the temperature is raised to 34 °C. Above 34 °C, the values of G' and G'' reach a plateau where $G' \sim G'' \sim 1.5$ mN/m. In parallel, it can be seen in Figure 3 that the bulk viscosity of the PNIPAM solutions experiences only minor changes in viscosity with a much different response profile. We observed a maximum in the bulk viscosity for $T = 30$ °C, which coincides with observations by Tam et al.[12] for more concentrated solutions. The authors attributed this behavior to the formation of a weak intermolecular gel across the sample. The different viscosity profile between the interface and volume with increasing temperature provides evidence that the strong increase in the interfacial moduli is a consequence of an increase in the surface

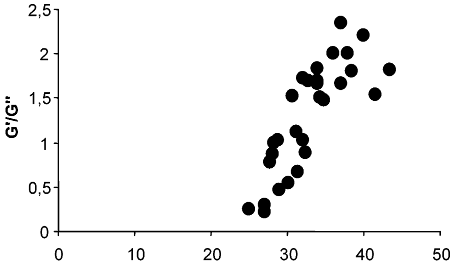

Figure 4. G'/G'' or tan ϕ for PNIPAM solutions (1 g/L, $M_w = 972\,500$ g/mol) as a function of temperature.

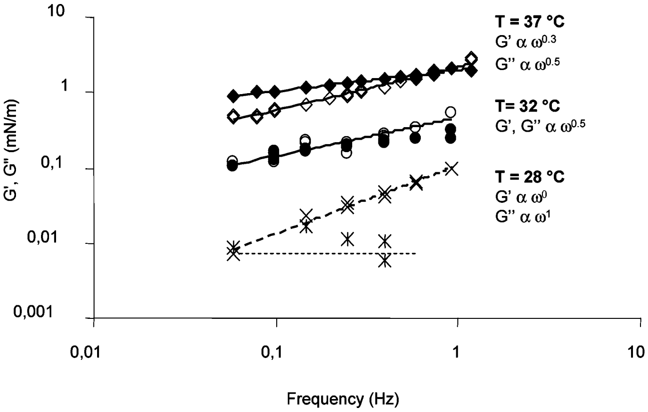

Figure 5. G' (full symbols) and G'' (open symbols) as a function of frequency for $T = 37$ (diamonds), $T = 32$ (circles), and $T = 28$ (squares).

viscoelasticity of the adsorbed layers and not fluid drag from the bulk solution onto the needle due to an increase in the solution's bulk viscosity. It should be specified that above the LCST the formation of a dense elastic surface layer was confirmed visually by the fact that it is possible to draw a thick membrane vertically from the surface using a needle. This phenomenon was not observed below the LCST.

Therefore, our results suggest a strong modification of the structure of the adsorbed layer with temperature. It should be noted that above the LCST, where most of the chains precipitate into macroscopic aggregates, we would rather expect a decrease in the surface rheological moduli as was observed by Monteux et al.[13] for biphasic oppositely charged polyelectrolyte−surfactant mixtures. However, the high surface moduli that we measure are consistent with Jean's neutron reflectivity results for this polymer,[7,9] which show a continuous increase in the thickness of the adsorbed layer and the amount of adsorbed molecules with temperature even above the LCST. As we will show later, the rheological behavior of the layer above the LCST strongly depends on the protocol used to heat the solutions.

Complementary information concerning the structure of the adsorbed layers can be gleaned from analyzing the ratio G'/G'' (or tan ϕ) as a function of temperature (Figure 4) as well as frequency measurements of G' and G'' (Figure 5). In Figure 4, it can be seen that the ratio G'/G'' increases from 0 to 2 when the temperature is raised from 20 to 45 °C. Below $T = 30-32$ °C, $G'/G'' < 1$, which is the sign that the layer has dominantly a viscous behavior. Above 32 °C, $G'/G'' > 1$, showing that the adsorbed layer is characterized by a more elastic behavior. This viscoelastic or liquid-to-solid transition is due to an increase of the density of the adsorbed layer and the number of entanglements. This also suggests the formation of physical links between molecules such as hydrogen bonds between adjacent acrylamide groups. However, the layer seems to behave like a rather soft physical gel since we have not observed any nonlinear effects, such as a yield stress. Also, the values of G' and G'' we measure are low compared to systems undergoing interfacial physical gelation, such as the lipopolymers studied by Naumann at the air−water interface, which form hydrogen bonds between ethylene oxide groups.[14]

In Figure 5, we report the values of G' and G'' as a function of the oscillation frequency $\omega = 0.005-1$ Hz, for $T = 28$, 32, and 37 °C (diamonds, circles, and crosses, respectively). At $T = 28$ °C, the values of G' are low and roughly independent of ω whereas $G'' \propto \omega^1$, which is typically characteristic of a Newtonian viscous surface layer. At $T = 37$ °C, $G' > G''$ and $G' \propto \omega^{0.3}$, $G'' \propto \omega^{0.5}$. The lower dependence of G' with frequency suggests a more rigid layer, since the rheological properties of a rubberlike layer are expected to be frequency independent. At the LCST, $G' \sim G'' \propto \omega^{0.5}$. The LCST thus represents the crossover temperature between a purely viscous and an elastic behavior.

3.2. Mechanism of Adsorption. 3.2.1. Influence of the Heating Protocol.

To better understand the mechanism of PNIPAM adsorption at the air−water interface, we have investigated the influence of the protocol used to heat the solutions. The three temperature cycles that we used are schematically represented in Figure 6a.

The results presented in section 3.1 correspond to a protocol that we call process 1, already described in section 3.1. Here the solution, first at ambient temperature, is then heated to the desired temperature. The surface rheological measurement is then carried out 1 h after the desired temperature is reached. To perform a measurement at a higher temperature, the thermostat is set to the corresponding temperature, usually 2 °C higher. As a result, the adsorbed layer is continuously being heated and ages from ambient temperature to 42 °C since the solution is not replaced. For example, for the highest temperatures investigated, the layer is about 8 h old. Thus, the increase in G' and G'' can result from a densification of the layer formed at the lowest temperatures in addition to the adsorption of more polymer as the solvent quality decreases with elevated temperature. In process 2, the solutions that are previously held at ambient temperature are heated as fast as possible up to the desired temperature (however, we do not control the speed of heating). The measurement is made 1 h after the temperature is reached. After the measurement, the solution is cooled to ambient temperature (it is verified that the surface moduli return to their initial values) and then heated again rapidly to the next temperature. Finally, in process 3, the solution is heated to the desired temperature. Then a fresh air−water surface is produced by aspiration of the surface using a pipet connected to a vacuum pump. This enables one to produce a fresh air−water interface directly at the desired temperature. The rheological measurement is then made 1 h after the aspiration. Therefore, in this last process, the adsorbed layer is 1 h old when the measurement is performed, and the layer is developed at the measurement temperature exclusively.

As can be seen in Figure 6b, the curve obtained using process 2 follows the curve of process 1 up to $T = 37$ °C. Above 37 °C, the values of G' and G'' obtained using process 2 decrease from 1.5 to 0.2 mN/m, unlike the results found with process 1 where they reach a plateau. G' and G'' measured using process 3 are similar to process 2 and process 1 until $T = 32$ °C where $G' = G'' = 0.4$ mN/m. Above 32 °C, G' and G'' decrease to 0.2 mN/m. Therefore, these results show that the heating process has a strong influence on the rheological properties and thus the structure of the PNIPAM layers. The highest values of G'

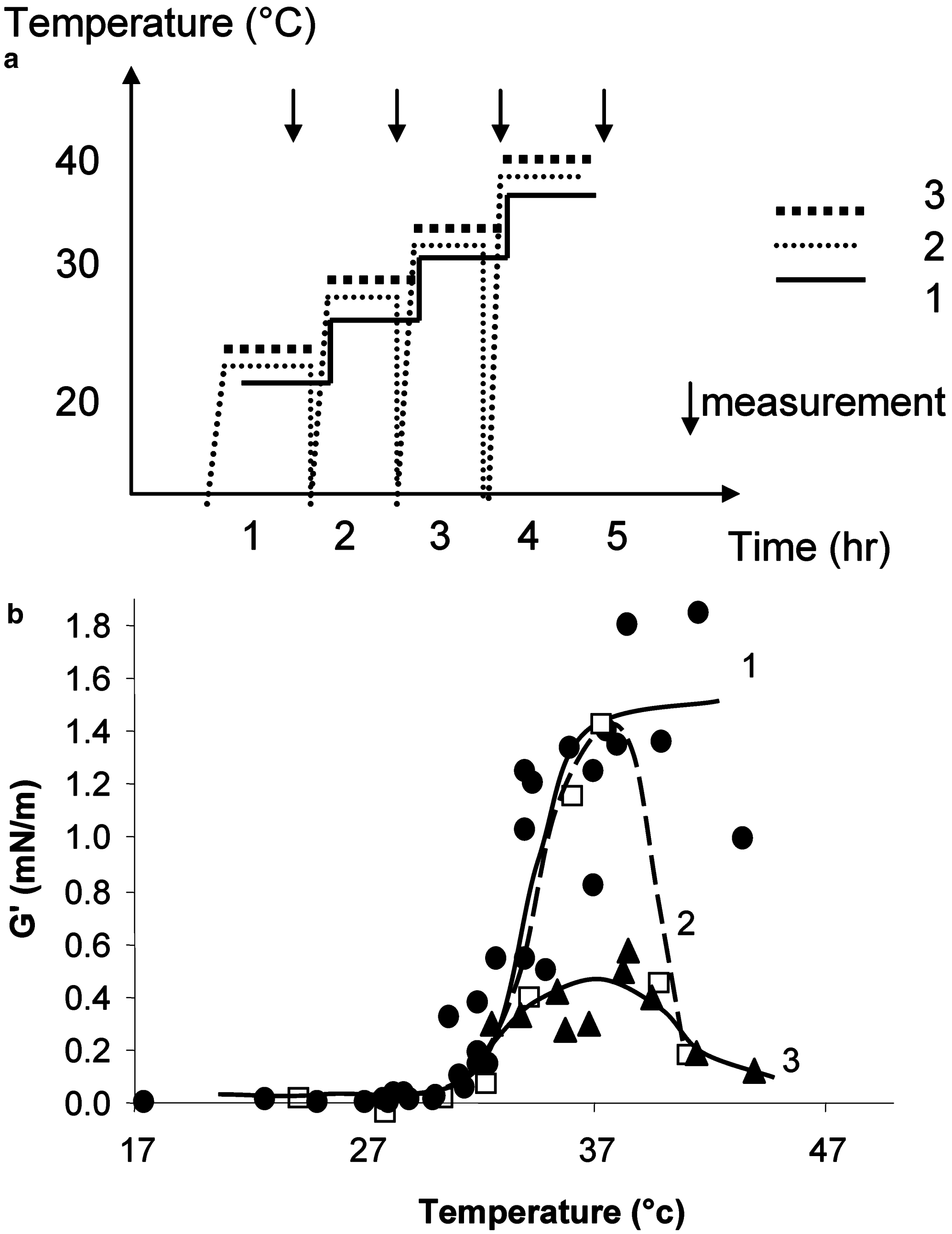

Figure 6. (a) Temperatures cycles corresponding to the three protocols used to heat the PNIPAM solutions. (b) G' as a function of temperature obtained for three different heating processes. Process 1 (full circles), process 2 (open squares), and process 3 (full triangles).

and G'' obtained with process 1 are most probably due to two effects: (1) As the temperature is increased, the layer formed at lower temperature becomes more compact since the quality of the solvent decreases. (2) Newly formed globules probably adsorb below this first layer acting as an anchor to form compact multilayers. A cartoon of the possible formation of these multilayers can be seen in Figure 7a. With process 3, integrated multilayers are probably not favorable because above the LCST, most of molecules precipitate into solid aggregates, which are not available for diffusion and adsorption to the interface. Therefore, the adsorption at the freshly formed air−water interface is probably lower in bad solvent conditions than in theta-solvent conditions. Surface rheological measurements as well as adsorption studies of diphasic solutions composed of oppositely charged polyelectrolytes and surfactants were performed by Monteux et al.[13,15] The authors have shown that when large macroscopic aggregates form in the solution, the adsorption is decreased and the surface shear moduli are very low. It was also found that under certain polymer concentrations it is possible to achieve a state where the adsorption is very high, but the shear surface moduli are very low because the interface is composed of large micrometric compact aggregates, which are loosely interconnected in the air−water interface. The low surface moduli that we measure at $T >$ LCST using process 3 are consistent with Monteux's results and show that in the biphasic region the adsorption is probably lower, and the layers have low interconnections likely due to the globular shape of the molecules[13] (see Figure 7b). Moreover, thick aggregates in thin liquid films of PNIPAM (same molecular weight and concentration) have also been reported by Jean et al.[7] The differences between these two processes show that the layers formed in process 1 are probably not in thermodynamic equilibrium and that the layers formed at low temperature are trapped at the interface when the temperature is raised. To have further information on nonequilibrium processes at the interface, scans of decreasing temperature scans would certainly be helpful

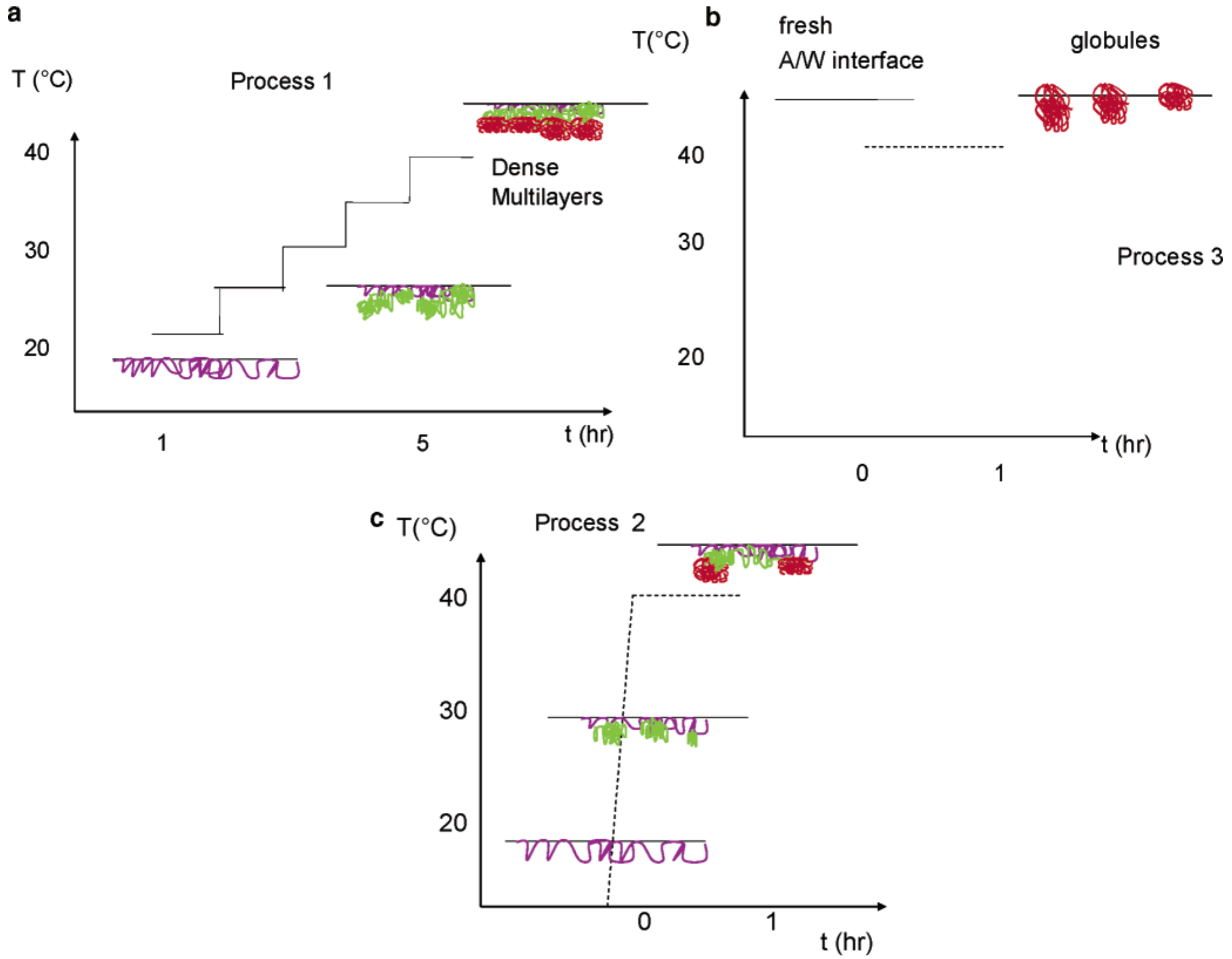

Figure 7. Schematic diagram of the adsorbed layers corresponding to various heating processes. (a) Process 1—continuous aging and heating of the adsorbed layers results in the formation of dense multilayers. (b) Process 3—a fresh interface is produced directly at the desired temperature. Above the LCST, the adsorption is lower and molecules form loosely connected globules. (c) Process 2—the heating phase from ambient to 40 is fast so that multilayers are less dense.

and are presently under way. Preliminary results show a hysteresis of G' and G''during temperature cycles.

On the basis of the above interpretation, the high G' and G'' measured using process 2 up to $T = 37$ °C are probably due to the fact that with this process the polymer layer spends a short time around the LCST. As the adsorption kinetics is rather fast (see next section), this short time spent around the LCST can be sufficient to induce multilayer formation and explains why up to 37 °C the results of processes 1 and 2 are similar. However, above 37 °C, the time frame at the LCST for process 2 conditions only results in looser multilayers that may easily unravel at higher temperature (Figure 7c).

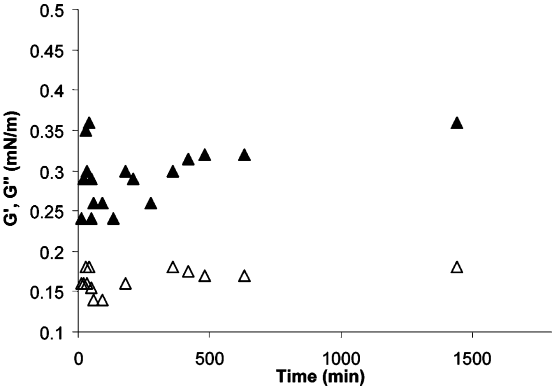

Figure 8. G' (full triangles) and G'' (open triangles) as a function of time for PNIPAM; $C = 1$ g/L (using process 1).

3.2.2. Adsorption Kinetics. For $T = 32$ °C, we have measured the values of G' and G'' as a function of time for more than 30 h (Figure 8). We found that G' (G'') increase from 0 to 0.35 mN/m (0.1) during the first 20 min after the temperature change and reach a plateau value for the next 30 h. Jean et al.[7] previously reported that the surface tension of PNIPAM solutions at the same concentration does not vary significantly after 200 s after the formation from a fresh interface. On the other hand, Noskov et al. reported nonmonotonic kinetics of the dilational elasticity of PNIPAM layers formed from very dilute solutions (from 10^{-9} to 10^{-4} wt %).[5] The authors explain this behavior by the fact that the dilute chains first have enough space to adsorb individually in flat layers, which produces an initial increase in the surface elasticity. At longer times, when the interface becomes more crowded, the chains start forming loops protruding in the solution, making the exchange of material easier upon compression/dilatation between the proximal and the central zone of the interface, resulting in a decrease in the surface elasticity. This result was predicted by a theoretical model.[16] Moreover, their study indicates that as the polymer concentration increases, the

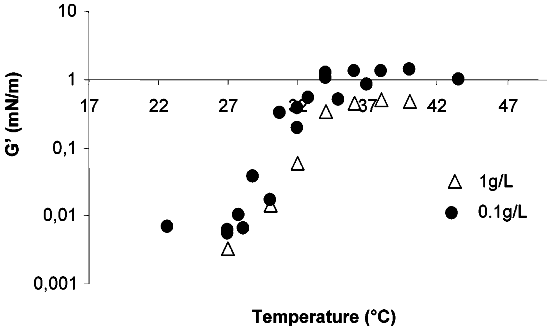

Figure 9. G' as a function of temperature for $C = 0.1$ g/L (open triangles) and $C = 1$ g/L (full circles) (using process 1).

maximum in surface elasticity becomes less pronounced and occurs at a very early stage after the formation of the interface. (The equilibrium elasticity is reached in less than 1 min for 0.1 wt % solutions vs 2 days for 10^{-9} wt % solutions.) In our study, we work with solution concentrations of 10^{-3} wt %. At these concentrations, Noskov et al. showed that the maximum in surface elasticity can occur very quickly and is barely noticeable. Moreover, the appearance of loops of polymer into the solutions might have a different consequence on the shear rheology of the layer than on the dilational rheology. The weak time dependence of the surface shear moduli as well as the surface tension indicates that the structure of the layer is not changing drastically with time. Our results suggest that a saturated and dense layer of PNIPAM forms rapidly at the air−water interface and does not rearrange significantly over time. This behavior is very different from other polymeric molecules such as proteins, which often show a logarithmic increase in the surface moduli over time due to rearrangements and interfacial gelation through the formation of intermolecular networks.[17]

3.3. Influence of PNIPAM Molecular Weight and Concentration. 3.3.1. Influence of PNIPAM Concentration and Compression. Figure 9 represents values of G' as a function of temperature for $C = 0.1$ and 1 g/L (open triangles and full circles, respectively) using process 1. It can be seen that the values of G' obtained with these two concentrations are in the same order of magnitude—the plateau value of G' are 0.5 mN/m when $C = 0.1$ g/L compared to 1.5 mN/m when $C = 1$ g/L. This result is consistent with Jean et al.'s study, which reports a low dependence of neutron reflectivity and surface tension with concentration above 10^{-4} g/L.[7]

In addition, we have performed measurements of G' and G'' upon compression of the layers using a Langmuir trough and compression barriers for $T = 32$, 34, and 36 °C. Upon compression, the surface tension measured using a Wilhelmy plate remains constant. More strikingly, the values of G' and G'' stay constant upon compression. This behavior is again very different from proteins, for which compression helps to form denser and more rigid layers, which is a sign of irreversibility of their adsorption. PNIPAM layers are composed of a very concentrated proximal layer and a more dilute thick central zone (several nanometers)[7,9] containing loops and tails. In comparison, proteins or polyelectrolytes, which are electrostatically charged, are more rigid molecules and do not have such a tendency to form loops. They form more rigid layers, which are much less compressible. The particular structure of PNIPAM layers explains the surprisingly weak effect of compression, consistent with the low elastic dilational moduli found by Noskov et al. for PNIPAM (at ambient temperature) as well as other nonionic polymers such as PVP and PEG.[18,19]

3.3.2. Influence of PNIPAM Molecular Weight. Figures 10 and 11 represent the evolution of G' as a function temperature using processes 1 and 2, respectively, for $M_w = 39$K, 76.5K, 186.5K, 465K, and 962K (full diamonds, open squares, full circles, crosses, and full circles, respectively) at a concentration equal to 0.1 g/L. As can be seen, when the molecular mass is increased by 2 orders of magnitude, the values of G' and G'' increased by less than a factor of 2 with both heating processes. Before the LCST, all molecular weights seem to give similar results. Above the LCST, the values of G' seem to show a maximum with M_w. It should be noticed that the polymers we used have rather high polydispersity indexes (up to 5 for the highest molecular weight), which might have an influence on our results. However, the highest molecular weights, $M_w = 962\,500$ and $M_w = 875\,400$, we used had two different polydispersity indexes (5.2 and 2.6) and nevertheless showed exactly the same behavior, leading us to think that the polydispersity does not change the global trends reported in this section.

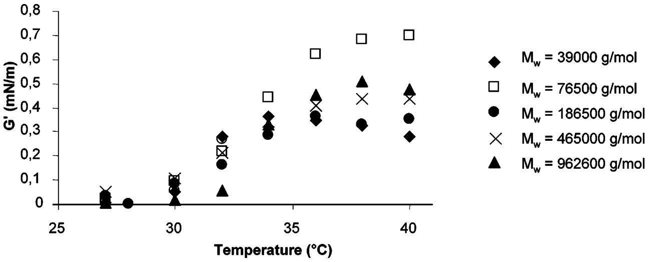

Figure 10. G' as a function of temperature using heating process 1 for PNIPAM solutions; $C = 0.1$ g/L, $M_w = 39\,000$ (full diamonds), 76 500 (open squares), 186 800 (full circles), 465 500 (crosses), and 962 600 (full triangles).

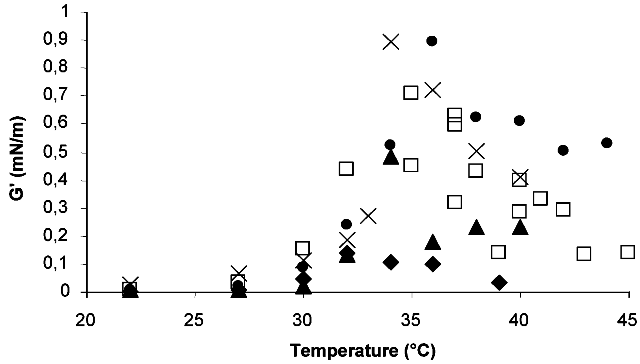

Figure 11. G' as a function of temperature using heating process 2 for PNIPAM solutions; $C = 0.1$ g/L, $M_w = 39\,000$ (full diamonds), 76 500 (open squares), 186 800 (full circles), 465 500 (crosses), and 962 600 (full triangles).

Figure 12 represents the value of G'/G'' as a function of temperature for the same five molecular weights investigated and using the heating process 1. It is worth noting that the results obtained for process 2 (not shown) show exactly the same trends. Most of the curves show a maximum of G'/G'' at a temperature equal to 32 °C. Also, the values of the ratios seem to show a maximum for $M_w = 465\,000$ g/mol.

We speculate that the nonmonotonic evolution of the rheological properties of the layer with the molecular mass may be due to the fact that it becomes easier to form entanglements at the interface, resulting in an increase in G' and G'' as well as G'/G'' with increasing molecular weight. However, very long chains possibly adsorb in a more globular state than short chains, which may form more heterogeneous and less dense layers. This would explain why we observe a fall in G', G'', and G'/G'' at high molecular weight.

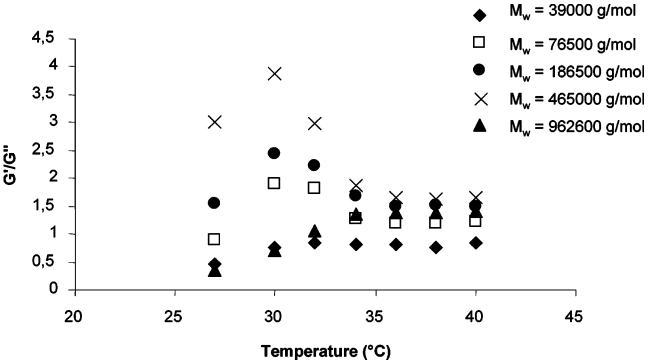

Figure 12. G'/G'' as a function of temperature using heating process 1 for PNIPAM solutions; $C = 0.1$ g/L, $M_w = 39\,000$ (full diamonds), 76 500 (open squares), 186 800 (full circles), 465 500 (crosses), and 962 600 (full triangles).

4. Summary and Conclusions

We found that PNIPAM layers adsorbed at the air–water interface show very specific features, which are summarized below:

(1) The surface rheology of PNIPAM is very sensitive to temperature. We observe a strong increase in the surface shear moduli as a function of temperature around the LCST although the bulk viscosity remains relatively low. Moreover, the layer undergoes a transition from a purely viscous layer to an elastic layer.

(2) The structure of the layers formed is very sensitive to the protocol used to heat the solutions. When the layers are continuously being heated from ambient temperature to 45 °C, we observe an increase in the surface shear moduli due to a densification of the first adsorbed layer as well as the possible adsorption of new globules (see Figure 7). The latter layer might not be at equilibrium but is however very stable. When a fresh interface is produced directly at a given temperature above the LCST, the surface is much less rigid. Indeed, above the LCST, most chains precipitate in a solid phase. The adsorption is thus limited. Moreover, molecules likely adsorb in a more globular state (weakly extended and entangled structure) at the interface resulting in low surface moduli.

(3) The structure of the layers is very weakly dependent on the molecular mass and the concentration. These features suggest the formation of a dense, saturated layer at the air–water interface. The surface rheology of the layer is not modified upon compression, suggesting that the layers are very compressible, due to the formation of loops and tails in the central zone of the layers.

(4) The adsorption of PNIPAM chains at the interface is fast, and the structure of the layers does not change significantly over long periods of time.

Being a neutral polymer, PNIPAM can form loops at the interface, resulting in soft and compressible layers. Also, the strong dependency of the rheological properties on the temperature history is certainly very interesting and has many practical implications.

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